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TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER
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U.S. APPLICATION NO. (if known, see 37 CFR 1.5)
10/049200

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/RU99/00294	13 August 1999	

TITLE OF INVENTION
Heat Accumulating Composition

APPLICANT(S) FOR DO/EO/US
SULZBACHER, Hartmut Hoehne et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. [x] This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. [] This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. [] This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(l).
4. [x] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [x] A copy of the International Application was filed (35 U.S.C. 371(c)(2))
   a. [x] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [] has been transmitted by the International Bureau.
   c. [] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [x] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [x] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [] have been transmitted by the International Bureau.
   c. [] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [x] have not been made and will not be made.
8. [] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. [] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [] A FIRST preliminary amendment.
    [] A SECOND or SUBSEQUENT preliminary amendment.
14. [] A substitute specification.
15. [x] A change of power of attorney and/or address letter.
16. [] Other items or information:

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Date of Deposit 08 Feb 2002

I hereby certify that this paper/fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to The Assistant Commissioner of Patents, Washington, D.C. 20231.

Administrator Mailing Application

Virginia C Byrd

Signature

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U.S. APPLICATION NO. (If known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
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				CALCULATIONS	PTO USE ONLY
ENTER APPROPRIATE BASIC FEE AMOUNT =				$740	
Surcharge of $130.00 for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				$0	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	12-20	0	x $18.00	$0	
Independent Claims	1-3	0	x $84.00	$0	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			$280.00	$0	
TOTAL OF ABOVE CALCULATIONS =				$740	
Processing fee of $130.00 for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				$0	
TOTAL NATIONAL FEE =				$740	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28,3.31). $40.00 per property +				$0	
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a. [ ] A check in the amount of $ ____ to cover the above fees is enclosed.

b. [x] Please charge my Deposit Account No. 16-2480 in the amount of $ 740 to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [x] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 16-2480. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

A. Winslow, Patent Attorney
Customer Number 27746

Signature

T. David Reed
Name
32,931
Registration Number

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HEAT ACCUMULATING COMPOSITION

Specification

Field of the Invention

The invention relates to supercooled heat accumulating materials with latent phase change heat, which can be used, for example, to warm parts of a human body, to warm up food or products and for other medical and household needs.

Background Art

In recent years a great deal of attention has been devoted to developing and using heat accumulating phase change materials and articles made on the base thereof. Phase change materials, capable of storing and generating heat, have found wide use in building materials, materials for road surfaces, containers for beverages and food products, in medical heating pads and in textile articles, for example, in clothes.

Known, for example, are phase change materials on the base of salts of nitrous and nitric acids, for example, of the following composition, % by weight:

sodium nitrite	40,
sodium nitrate	7,
potassium nitrate	53.

This composition melts at 142°C with a specific heat of the phase transition equal to 81.4 kJ/kg [Une V.W., Voznick H.P. Molten Salt as a Heat Transfer Medium – Chemical Engin. Progress. 1963, vol. 59, N 5, p. 35].

In order to reduce the level of the working temperature and to increase the energy capacity, this composition was modified by the addition of sodium acetate and had the following composition, % by weight:

sodium nitrite	39.7-41.4,
sodium nitrate	50.5-52.7,
sodium acetate	5.9-9.8.

This composition melts at 124-130°C with a specific heat of the phase transition equal to 126-132 kJ/kg [USSR Inventor's Certificate 1733461 A1, 1990, IPC^5 C 09 K /06].

Sodium acetate in the form of a trihydrate is one of the earliest and most well-studied heat-accumulating materials. Its supersaturated solutions may be cooled to a temperature below 0°C, retaining therewith a reserve of latent energy. This energy may be preserved for a long time without degradation or spontaneous release, and upon initiation it may be generated at any moment. Sodium acetate trihydrate is very convenient in those cases when it is necessary to rapidly raise the temperature to 50°C.

A supercooled heat-accumulating material on the base of sodium acetate trihydrate was proposed with gelatin as the plasticizer, in the following composition:

sodium acetate trihydrate	97.50-99.95,
gelatin	0.05-2.50.

The energy capacity of this material is 250-260 kJ/kg, the number of thermal cycles without reduction of the energy capacity – not less than 1000, while the temperature of the heating pad 20 sec after initiation is 57-58°C [USSR patent 1833404 A3, priority date February 6, 1990, IPC^5 C 09 K /06].

However, when the known compositions are used for medical purposes, for example, as a source of heat in medical heating pads, a problem exists which is related to the heating temperature of the heat-accumulating material, which may result in burns, and consequently, cannot be used without appropriate protection means, etc.

Such a heat-accumulating material is desirable for medical heating pads, which would have a phase change temperature close to the body temperature of a human (ideally about 36-42°C), which after initiation would generate heat for a long period (ideally 4 hours and more), which would maintain stability in a supercooled state at temperatures from room temperature to –20°C, and which would retain its properties during multiple use.

A heat-accumulating material, which also has a phase transition at a temperature close to the temperature of a human body, self-crystallizing, capable of retaining a predetermined temperature for a lengthy period due to the heat of crystallization and not losing its properties during repeated use, is suitable for medical purposes related to the necessity of maintaining stable heating temperature over a lengthy period.

Also known are compositions which comprise gum arabic, paraffin etc., but their capability of prolonging the period of heat generation has never been discussed. To the contrary, the presumption was made that they promote initiation of crystallization

(PCT/AU93/00427 and Ulman and Valentin, Solar Energy Materials, vol. 9, 177-181, 1983), i.e. that they have an opposite effect.

The object of the present invention is to develop a material which conforms with the requirements indicated above.

Description of the Invention

The authors of the present invention showed that use of a crystallization modifier makes it possible to prolong the time heat is generated by the heat-accumulating composition and modifies the stability of the supercooled state.

The Applicants also showed that the proposed compositions also have such a positive property as the possibility for their multiple use.

Thus, the present invention relates to a heat-accumulating composition comprising a phase change material and a crystallization modifier, taken in a predetermined ratio, which has a liquid-solid phase transition temperature, close to the temperature of a human body.

More concretely, the invention relates to a heat-accumulating composition comprising a phase change material with a range of the liquid-solid phase transition temperature, and a crystallization modifier, taken in the following ratio, % by weight:

phase-change material	95-99.9,
crystallization modifier	0.1-5.0.

Different compositions, which have a range of the liquid-solid phase transition temperature equal to 34-56°C, may be used as the phase-change material. Such compositions may be, for example, a mixture of sodium acetate trihydrate and sodium thiosulfate pentahydrate, sodium acetate trihydrate and urea; a mixture of magnesium nitrate hexahydrate, magnesium chloride hexahydrate and ammonium nitrate; mixtures of acetamide and potassium acetate, ammonium nitrate or urea; mixtures of urea and sodium bromide, potassium isothiocyanate, sodium iodide or sodium nitrate.

Paraffin, gum arabic, gelatin or other organic substances, for example, which have plasticizing or jellying properties, may be used as a crystalline modifier.

In particular, it is proposed that a mixture of sodium thiosulfate pentahydrate and sodium acetate trihydrate, taken in the following ratio, % by weight:

$CH_3COONa.3H_2O$	28-50,
$Na_2S_2O_3.5H_2O$	50-72,

be used as the phase change material.

An example may be a composition comprising 28% of a first component and 72% of a second, which meets eutectics, formed by sodium acetate trihydrate and sodium thiosulfate pentahydrate. The mixture melts within the range of from 38 to 56°C. In accordance with differential scanning calorimetry (DSC), the enthalpy of melting was 201.29 J/g at a temperature of 40.3°C maximum, crystallization was not observed when cooled to -20°C. The temperature range of 37-41°C is reached when crystallization of a melt weighing 20-70 g is initiated. The duration of heat generation at body temperature is, depending on weight, from 50 minutes to 3 hours. At room temperature, the duration of heat generation is reduced two times.

The optimum additive is paraffin. The amount of the additive is 0.2-0.5% of the weight of the mixture. In the presence of a 0.5% paraffin additive, the heating temperature of the mixture does not differ from that of a pure mixture, while the duration of heat generation is increased two times. When the weight of the mixture is 50 g, heat generation at human body temperature is retained for 5 hours. Multiple repetition of the melting-hardening cycles under rarefaction conditions < 10 mm Hg has no influence on the heating characteristics of this mixture. After 20 cycles, the heating temperature of a 50 g mass is 40.5°C with a 5-hour duration of heat generation, among which the temperature exceeds 39°C during 3.5 hours.

Melting a mixture comprising 50% $CH_3COONa.3H_2O$ and 50% $Na_2S_2O_3.5H_2O$ takes place within the temperature range of 37-36°C, the melting enthalpy is, according to DSC data, 218.7 J/g at a temperature 41°C maximum. The maximum temperature of the mixture during crystallization of a melt weighing 10-100 g is 40.5-47°C. The duration of heat generation depends on the ambient temperature. At human body temperature, heat generation continues for from 1 to 3 hours for the aforesaid weight. Multiple repetition of the melting-hardening cycles under rarefaction conditions ≤ 10 mm Hg does not affect the heating characteristics of this mixture. Being melted, the mixture is retained in a liquid form for a lengthy period.

Another example of a phase change material comprising sodium acetate trihydrate is a mixture of sodium acetate trihydrate and urea, taken in the following ratio. % by weight:

$CH_3COONa.3H_2O$	75-90,
NH_2CONH_2	10-25.

Compositions, consisting of sodium acetate trihydrate and urea are interesting in that the temperature to which they heat, when crystallization of one and the same weight is initiated, is reduced in proportion to the increase in the content of urea therein. By changing the content of urea in the mixture from 10 to 35% and the weight from 20 to 100g, it is possible to obtain any heating temperature of the mixture within the range of from 32 to 50°C.

According to DSC data, two heating effects are noted for a composition comprising 15% urea: with a maximum at 34.3°C and enthalpy 71.48 J/g, with a maximum at 49.1°C and enthalpy 91.18 J/g, crystallization is not observed when cooled to –20°C. The melting range of this composition is substantially increased: 30.5-60.5°C. When the urea content increases, the melting range becomes somewhat narrower, while the heating effect is reduced. The duration of heat generation of these mixtures hardly changes at all when the composition changes and is determined by the weight: at a weight of 20-70 g the duration of action of the composition is 1-3 hours.

A mixture containing 20% urea, weight 50 g, is heated to 42°C. The optimum additive is gum arabic, which may be introduced in the form of a powder and in the form of a solution in water. The amount of gum arabic is 0.1-0.21% of the weight of the mixture. In the presence of this additive, the maximum heating temperature of the mixture with a weight of 50 g and multiple heat cycling is 44-45°C. The duration of heat generation at human body temperature is 3.5-4 hours, among which the temperature is above 38°C for approximately 2 hours.

One more example of a phase change material is a mixture of magnesium nitrate hexahydrate, magnesium chloride hexahydrate and ammonium nitrate, taken in the following ratio, % by weight:

$Mg(NO_3)_2.6H_2O$	30.6,
$MgCl_2.6H_2O$	31.9,
NH_4NO_3	37.5.

This composition is triple eutectic, melting in a range of from 42 to 53.5°C. According to DSC data, the melting enthalpy is 118.89 J/g with a maximum at 44.5°C, when cooled to −20°C the effects were not observed. In the case of rapid cooling, spontaneous crystallization is observed at 42.5°C...A mixture weighing 20-60 g heats to 42-45°C. The duration of heat generation is from 1.5 to 3.5 hours.

Paraffin, gum arabic or gelatin, in particular, may be used as the crystalline modifier.

This mixture may be used to stabilize the heating temperature at a level which is safe for a human body.

It is also proposed that mixtures on the base of acetamide be used as the heat-accumulating phase change material, in particular:

a mixture of acetamide and potassium acetate, taken in the following ratio, % by weight;

CH_3CONH_2	67,
CH_3COOK	33;

a mixture of acetamide and urea, taken in the following ratio, % by weight;

CH_3CONH_2	65,
NH_2CONH_2	35;

a mixture of acetamide and ammonium nitrate, taken in the following ratio, % by weight;

CH_3CONH_2	65,
NH_4NO_3	35.

The last mixture is an eutectic composition which has a phase transition at a melting temperature of 36-41°C. According to DSC data, enthalpy of the transition is 141.28 J/g with a maximum at 38°C, upon cooling an effect is detected at −13.3°C with an enthalpy of 77.18 J/g.

In the case of rapid cooling in air, spontaneous crystallization takes place at 29-35°C. The speed of crystallization at temperatures close to 36°C is very low, which ensures lengthy, soft heat generation. The heating temperature of a mixture weighing 20-50 g is 39-43°C. The duration of heat generation with a weight of 20-50 g at a temperature of 36°C is from 3 to 6 hours.

An additive may be paraffin. In the presence of 0.5% paraffin at a temperature of 36.6°C, the heat generation is more energetic but less prolonged.

Thus, the instant composition may be utilized for stabilization of the heating temperature in a medical device at a level which is not dangerous for a human being. This device should not be initiated at room temperature, but directly before utilization may be heated over a water bath until the mixture is completely dissolved. After cooling and the beginning of crystallization, the device is applied to the necessary part of the body. Because of the large heat capacity, the heating bag cools very slowly, and after cooling to a temperature below body temperature, spontaneous crystallization with heat generation begins again.

It is proposed that compositions consisting of mixtures of urea and inorganic salts also be used as phase change materials spontaneously crystallizing in the process of cooling.

Urea may be included in the composition of phase change material in the form of a mixture of urea and sodium bromide, taken in the following ratio, % by weight:

NH_2CONH_2	69.3,
NaBr	30.7;

a mixture of urea and potassium isothiocyanate, taken in the following ratio, % by weight:

NH_2CONH_2	53.2,
KCNS	46.8;

a mixture of urea and sodium iodide, taken in the following ratio, % by weight:

NH_2CONH_2	62.3,
NaJ	37.7;

a mixture of urea and sodium nitrate, taken in the following ratio, % by weight:

NH_2CONH_2	46.5,
NH_4NO_3	53.5.

These mixtures are eutectics, formed in according systems on the base of urea. The melting range of the mixtures is 34-47°C. The mixtures of urea and sodium bromide, sodium nitrate and potassium thioisocyanate crystallize spontaneously when cooled in air at temperatures of 30-38°C. The mixture of urea and sodium iodide crystallizes in different manners depending on the cooling conditions: from spontaneous crystallization to supercooling to –20°C.

These mixtures are recommended for utilization as heat accumulating materials in order to stabilize the temperature at a level close to the temperature of a human body.

The Applicants have shown that multiple repetition of the melting to hardening cycles for the proposed heat accumulating compositions does not affect their heat characteristics. This is a positive property and makes it possible to use them a multiple number of times.

The examples presented below illustrate the proposed invention, but do not in any manner restrict it.

Example 1. Composition: 28% $CH_3COONa.3H_2O$ + 72% $Na_2S_2O_3.5H_2O$.

A mixture of 50 g total weight, consisting of 28% by weight of $CH_3COONa.3H_2O$ and 72% of $Na_2S_2O_3.5H_2O$ is carefully ground and mixed. A paraffin additive is introduced in an amount of 0.5% or gum arabic in an amount of 1-3% of the weight of the mixture in the form of finely ground powder and carefully mixed. The obtained mixture is placed in a glass vessel provided with a mechanical initiator, with a cock for vacuumizing the vessel and with a thermocouple. Air is pumped out of the vessel, then it is heated over a water bath at a temperature of 80-90°C until the smallest crystals of the mixture are completely melted (not less than 30 minutes). The melted mixture is cooled and initiated. By means of the thermocouple and a recorder, the heat generation curve of the mixture in time is registered. During the initiated crystallization of a mixture weighing 20-70 g, the heating temperature reaches 37-41°C. The duration of heat generation at body temperature reaches 5 hours.

In Table 1, presented below, data is presented on the temperature and heating duration of a mixture weighing 50 g, retaining the gum arabic and paraffin additives. Figures 1 and 2 show the heat generation curves with mixtures having additives of 0.5% paraffin or 3% gum arabic after multiple repetition of the melting-crystallization cycles.

Table 1

28% $CH_3COONa.3H_2O$ + 72% $Na_2S_2O_3.5H_2O$,
temperature in a constant-temperature chamber 36.6°C,
weight of the mixture – 50 g

Additive	Heat cycling, times	T_{max}, °C	Time, hours
1% gum arabic	1	40.3	4 hours 40 min
3% gum arabic	5	40.7	5 hours 10 min
3% gum arabic	10	40.8	4 hours 30 min
3% gum arabic	15	40.7	4 hours 30 min
0.5% paraffin	1	40	5 hours

0.5% paraffin	5	41	4 hours 40 min
0.5% paraffin	10	41	4 hours 30 min
0.5% paraffin	15	40.5	5 hours 24 min
0.5% paraffin	20	40.4	5 hours

Example 2. Composition: 80% $CH_3COONa.3H_2O$ + 20% $CO(NH_2)_2$.

The method for preparing the mixture and determining its heat generating characteristics is similar to that indicated in Example 1.

An addition of 2% gum arabic is introduced in the form of a 15% solution into the melt of a finished mixture after cooling. Before utilization the finished mixture is initiated.

In Table 2, presented below, data is provided on the temperature and duration in which a mixture weighing 50 g heats in the presence of different additives. Heat generation curves of the mixture in the presence of paraffin and gum arabic additives are presented in Figs. 3-4.

Table 2

80% $CH_3COONa.3H_2O$ + 20% $CO(NH_2)_2$,

temperature in a constant-temperature chamber 36.6°C

Additive	Heat cycling, times	T_{max}, °C	Time, hours
	-	42	2 hours
0.5% paraffin	1	42	1 hour 50 min
0.5% paraffin	6	44	2 hours 40 min
0.5% paraffin	Γ0	45	2 hours 50 min
0.2% gum arabic	1	44.5	3 hours 40 min
0.2% gum arabic	6	44.5	3 hours 20 min
0.2% gum arabic	11	43	3 hours
2% gum arabic	1	42.5	3 hours
2% gum arabic	5	45	3 hours 50 min
2% gum arabic	10	45.5	3 hours 55 min
2% gum arabic	20	45	3 hours 20 min

Example 3. Composition 30.6% $Mg(NO_3)_2.6H_2O$ + 31.9% $MgCl_2.6H_2O$ + 37.5% NH_4NO_3

The mixture is prepared in a manner similar to that indicated in Example 1. After melting, the finished mixture is cooled in air. In the process of cooling, crystallization begins spontaneously at a temperature of 40-42°C. The heating temperature of a mixture of 60 g weight is 45°C (Table 3), the duration of heat generation – 3.5 hours. In the presence of gelatin and gum arabica additives, the heating temperature drops somewhat, while the duration increases.

Table 3

30.6% $Mg(NO_3)_2.6H_2O$ + 31.9% $MgCl_2.6H_2O$ + 37.5% NH_4NO_3 ,

temperature in a constant-heat chamber 36.6°C

Additive	Weight, g	T_{max}, °C	Time
-	20	43	1 hour 20 min
-	40	43.5	2 hours 50 min
-	60	45	3 hours 30 min
5% gelatin	20	38.5	1 hour 30 min
5% gum arabica	20	39.5	1 hour 30 min

This mixture was used as a heat-stabilizing sublayer for a heat-generating Fe-comprising composition (Fig. 5). With a ratio of the weight of the sublayer to that of the heating composition equal to 1:1, the temperature at the beginning of melting--42°C--remained practically constant and did not increase during further heating. During cooling the heat generation is prolonged due to the heat of crystallization. This mixture makes it possible to maintain the heating temperature--37-43°C--for 7 hours. The heat generating curve has a plateau.

Example 4. Composition: 65% CH_3CONH_2 + 35% NH_4NO_3

The method of preparing the mixture is similar to that of example 1. After melting, the finished mixture is cooled in air prior to the beginning of spontaneous crystallization. The heat generation curve of a mixture with a weight of 35 g and an additive of 0.5% wax is presented in Fig. 6. The maximum heating temperature is 40°C, the duration of heat

generation is 4 hours, among which the temperature is stably maintained at the 37°C level for more than two hours.

Similar results were also obtained when this mixture was used as a heat-stabilizing sublayer for a heat generating Fe-comprising composition (Fig. 7). With the ratio of the weight of the sublayer to that of the heating composition equal to 1:2, the heating temperature does not exceed 37°C, while the duration of the heating at the > 36°C level is 4 hours.

Example 5. Composition: 69.3% NH_2CONH_2 + 30.7% NaBr and

53.2% NH_2CONH_2 + 46.8% KCNS.

The mixture is prepared in a manner similar to example 1. The obtained mixture was used as a heat-stabilizing sublayer for a heat-generating Fe-comprising composition. Fig. 8 shows the influence of a sublayer of the mixtures indicated above on the heating of a heat-generating Fe-comprising composition. When used as a sublayer, these mixtures make it possible to reduce the heating temperature to 42-44°C. An increase in the duration of heat generation is achieved by generating heat during spontaneous crystallization in the cooling process. A mixture with the inclusion of potassium thiocyanate makes it possible to obtain more uniform heating, this being shown by the plateau on the heat generating curve, but the weight of the salt mixture in that case should be somewhat greater than the weight of the heating mixture. Thus, the eutectics of urea with potassium thiocyanate and sodium bromide may be used for heat stabilization of the temperature within the range of 40-44°C for 4 hours.

Example 6.

This example illustrates the effect of additives of gum arabica and gelatin on the duration of heat generation during crystallization of heat accumulating mixtures with a phase transition. Fig. 9 shows heat generating curves of a composition consisting of 28% $CH_3COONa.3H_2O$ and 72% $Na_2S_2O_3.5H_2O$ without additives and in the presence of additives – 5% gum arabica and 5% gelatin. Curve 1 corresponds to the heat generation of a mixture without additives. The introduction of additives (curves 2, 3) increases the duration of heat generation of a 20 g mixture by 1.5 times. In Fig. 10, a heat generation curve corresponding to a mixture of 85% $CH_3COONa.3H_2O$ + 15% $CO(NH_2)_2$ without additives (1) is compared with a curve for that same mixture in the presence of 5% gelatin (2). An increase of the duration of heat generation in this case is even more noticeable.

SET OF CLAIMS

1. A heat-accumulating composition comprising a phase change material, with a range of the liquid-solid phase transition temperature equal to 34-56°C, and a crystallization modifier, taken in the following ratio, % by weight:

phase change material	95-99.9,
crystalline modifier	0.1-5.0.

2. A composition according to claim 1, characterized in that the phase change material is a mixture of sodium acetate trihydrate and sodium thiosulfate pentahydrate, taken in the following ratio, % by weight:

$CH_3COONa.3H_2O$	28-50,
$Na_2S_2O_3.5H_2O$	50-72.

3. A composition according to claim 1, characterized in that the phase change material is a mixture of sodium acetate trihydrate and urea, taken in the following ratio, % by weight:

$CH_3COONa.3H_2O$	75-90,
$CO(NH_2)_2$	10-25.

4. A composition according to claim 1, characterized in that the phase change material is a mixture of magnesium nitrate hexahydrate, magnesium chloride hexahydrate and ammonium nitrate, taken in the following ratio, % by weight:

$Mg(NO_3)_2.6H_2O$	30.6,
$MgCl_2.6H_2O$	31.9,
NH_4NO_3	37.5.

5. A composition according to claim 1, characterized in that the phase change material is a mixture of acetamide and potassium acetate, taken in the following ratio, % by weight;

CH_3CONH_2	67,
CH_3COOK	33.

6. A composition according to claim 1, characterized in that the phase change material is a mixture of acetamide and ammonium nitrate, taken in the following ratio, % by weight;

CH_3CONH_2	65,
NH_4NO_3	35.

7. A composition according to claim 1, characterized in that the phase change material is a mixture of acetamide and urea, taken in the following ratio, % by weight;

CH_3CONH_2	65,
NH_2CONH_2	35.

8. A composition according to claim 1, characterized in that the phase change material is a mixture of urea and sodium bromide, taken in the following ratio, % by weight:

NH_2CONH_2	69.3,
NaBr	30.7.

9. A composition according to claim 1, characterized in that the phase change material is a mixture of urea and potassium isothiocyanate, taken in the following ratio, % by weight:

NH_2CONH_2	53.2,
KCNS	46.8.

10. A composition according to claim 1, characterized in that the phase change material is a mixture of urea and sodium iodide, taken in the following ratio, % by weight:

NH_2CONH_2	62.3,
NaJ	37.7.

11. A composition according to claim 1, characterized in that the phase change material is a mixture of urea and sodium nitrate, taken in the following ratio, % by weight:

NH_2CONH_2	46.5,
NH_4NO_3	53.5.

12. A composition according to claim 1, characterized in that paraffin, gum arabic, gelatin, wax and other organic products that have jellying or plasticizing properties are used as the crystallization modifier.

1004920D .030702

(12) МЕЖДУНАРОДНАЯ ЗАЯВКА, ОПУБЛИКОВАННАЯ В СООТВЕТСТВИИ С ДОГОВОРОМ О ПАТЕНТНОЙ КООПЕРАЦИИ (PCT)

(19) ВСЕМИРНАЯ ОРГАНИЗАЦИЯ ИНТЕЛЛЕКТУАЛЬНОЙ СОБСТВЕННОСТИ
Международное бюро

PCT

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(71) Заявитель *(для всех указанных государств, кроме (US):* **PROCTER & GAMBLE COMPANY** [US/US]; One Procter & Gamble Plaza, Cincinnati, (US).

(72) Изобретатели; и
(75) Изобретатели/Заявители *(только для (US):* **ДЯТЛОВ Валерий Александрович** [RU/RU]; 119034 Москва, Малый Левшинский переулок, д. 12, кв. 6 (RU) [**DYATLOV, Valery Alexandrovich**, Moscow (RU)]. **HARTMUT, Hoehne** [DE/DE]; Sulzbacher str. 40-50, D-65842 Schwalbach am Taunus (DE). **ВИНОГРАДОВ Валентин Антонович** [RU/RU]; 123007 Москва, Хорошевское шоссе, д. 34, кв. 38 (RU) [**VINOGRADOV, Valentin Antonovich**, Moscow (RU)]. **КРЕНЕВ Владимир Александрович** [RU/RU]; 109377 Москва, Зеленодольская ул., д. 7, корп. 2, кв. 71 (RU) [**KRENEV, Vladimir Alexandrovich**, Moscow (RU)]. **ДРОБОТ Наталья Фёдоровна** [RU/RU]; 125319 Москва, Красноармейская ул., д. 25, кв. 57 (RU) [**DROBOT, Nataliya Fedorovna**, Moscow (RU)]. **ГАВРИЧЕВ Константин Сергеевич** [RU/RU]; 117334 Москва, Ленинский проспект, д. 30, кв. 165 (RU) [**GAVRICHEV, Konstantin Sergeevich**, Moscow (RU)]. **БАБИЕВСКАЯ Ирина Зиновьевна** [RU/RU]; 117454 Москва, проспект Вернадского, д. 24а, кв. 37 (RU) [**BABIEVSKAYA, Irina Zinovievna**, Moscow (RU)]. **НОСКОВА Ольга Анатольевна** [RU/RU]; 144007 Московская обл., Электросталь, ул. Мира, д. 11а, кв. 4 (RU) [**NOSKOVA, Olga Anatolievna**, Elektrostal (RU)]. **БАЖЕНОВА Елена Владимировна** [RU/RU]; 127238 Москва, Дмитровское шоссе, д. 55, кв. 33 (RU) [**BAZHENOVA, Elena Vladimirovna**, Moscow (RU)]. **ВАСИЛЬЕВ Виктор Сергеевич** [RU/RU]; 125422 Москва, ул. Тимирязевская, д. 7, кв. 73 (RU) [**VASILIEV, Viktor Sergeevich**, Moscow (RU)].

(74) Агент: ООО «ГОРОДИССКИЙ И ПАРТНЁРЫ»; 129010 Москва, ул. Б.Спасская, д. 25, строение 3 (RU) [**ООО «GORODISSKY I PARTNERY»**, Moscow (RU)].

(81) Указанные государства *(национально):* AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW.

(84) Указанные государства *(регионально):* ARIPO патент (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), евразийский патент (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), европейский патент (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), патент OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

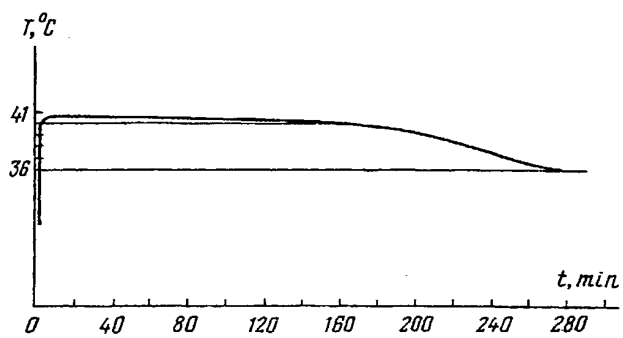
Опубликована
С отчётом о международном поиске.

В отношении двухбуквенных кодов, кодов языков и других сокращений см. «Пояснения к кодам и сокращениям», публикуемые в начале каждого очередного выпуска Бюллетеня PCT.

(54) Title: THERMAL STORAGE COMPOSITION

(54) Название изобретения: ТЕПЛОАККУМУЛИРУЮЩАЯ КОМПОЗИЦИЯ

(57) Abstract: The invention relates to a thermal storage composition containing a phase transition material having a range of temperatures corresponding to the liquid - solid phase transition ranging between 34 and 56 °C and a crystallization modifier represented in the following proportions, in weight percent: phase transition material 95 - 99.9; and crystallization modifier 0.1 - 5.0.



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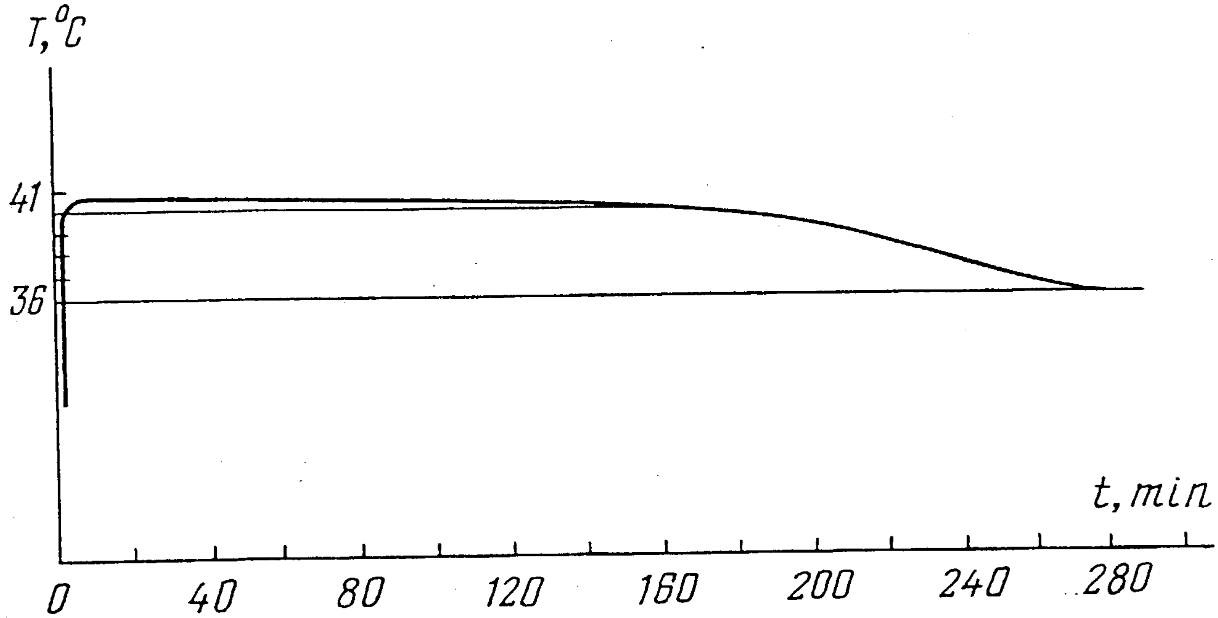
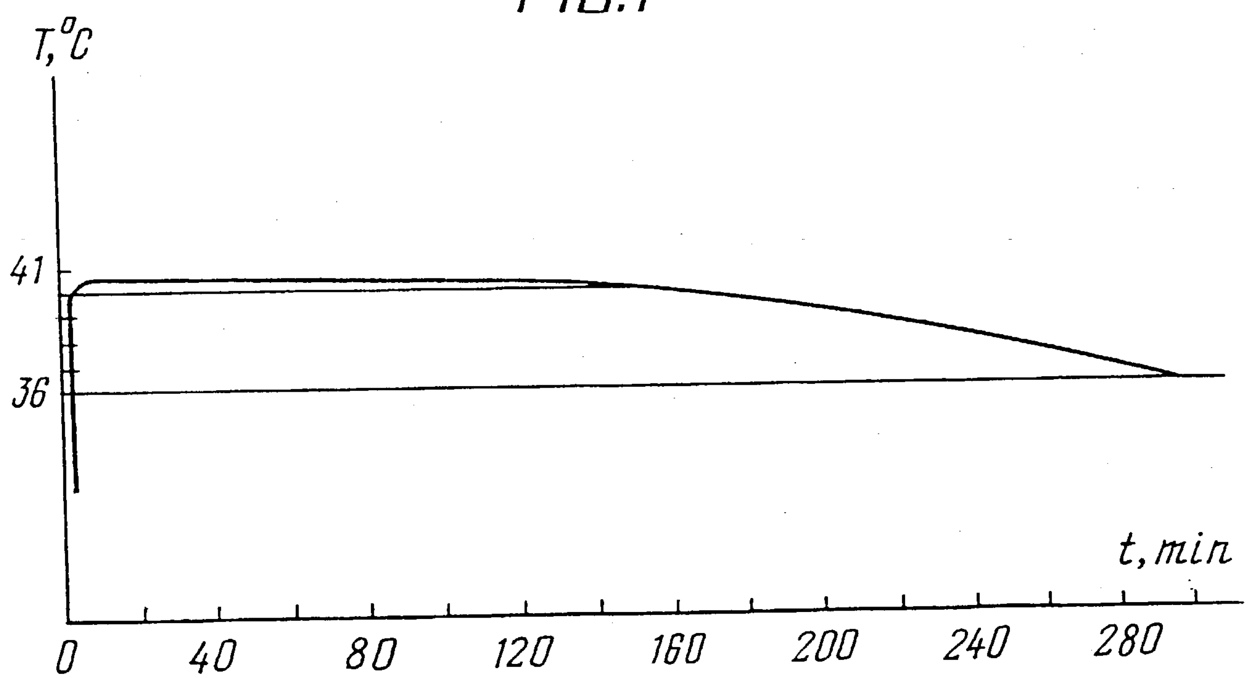

T, °C
41
36
t, min
0
40
80
120
160
200
240
280

FIG.1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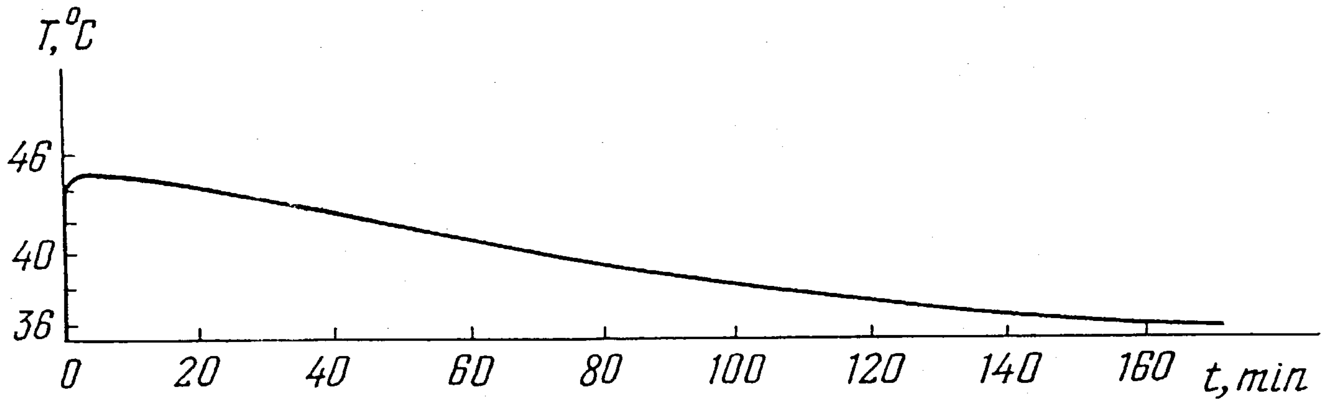
36
t, min
0
40
80
120
160
200
240
280

FIG.2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46
40
36
0
20
40
60
80
100
120
140
160
t, min

FIG. 3

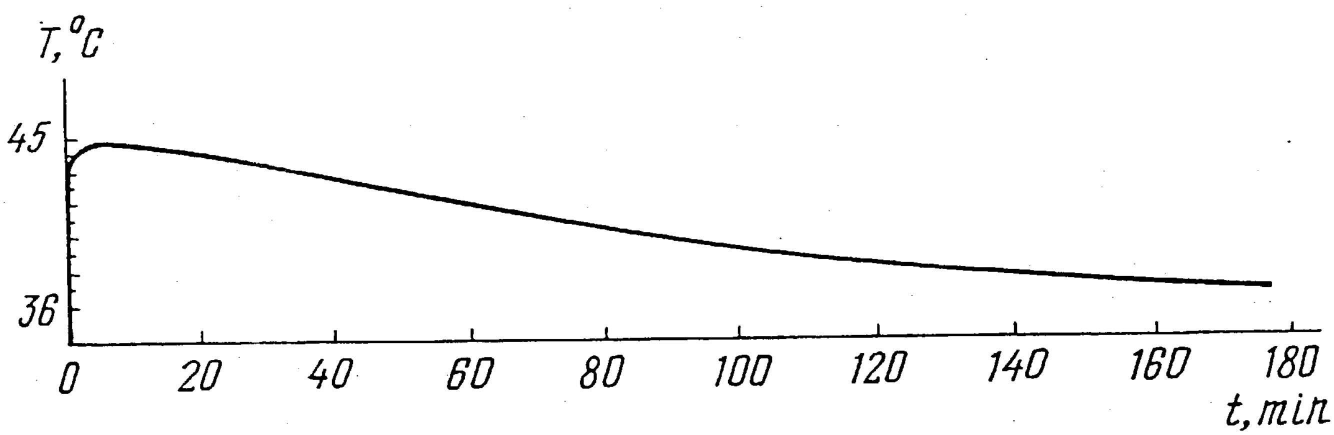
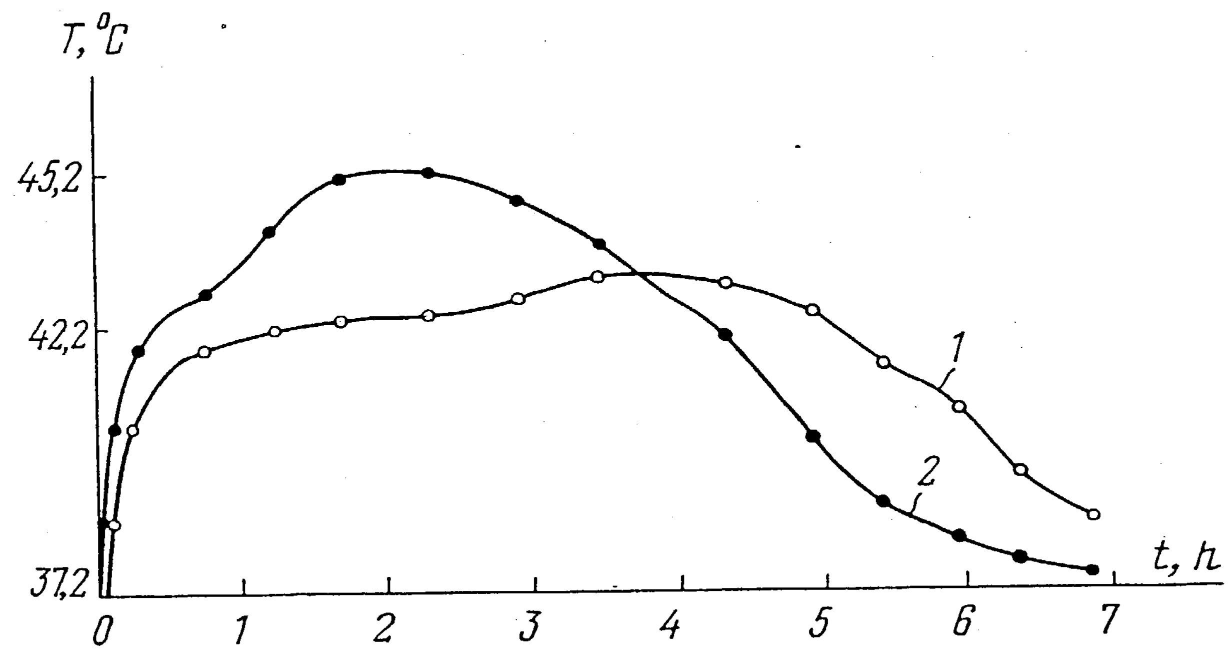

T, °C
45
36
0
20
40
60
80
100
120
140
160
180
t, min

FIG.4


T, °C
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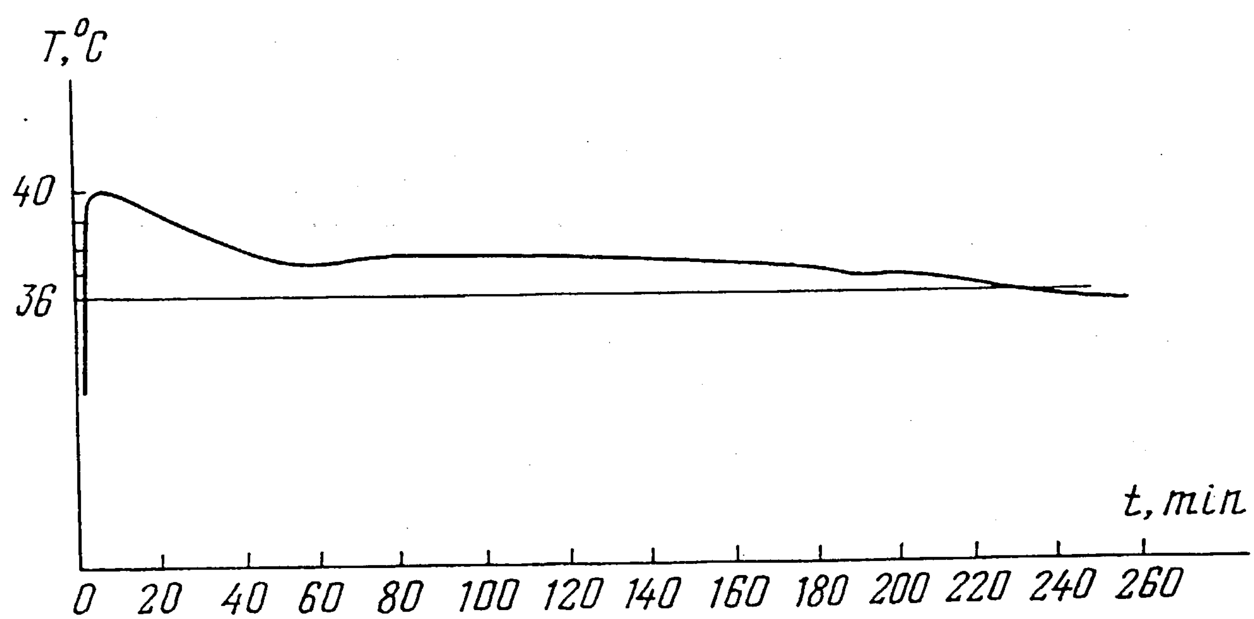
42,2
37,2
0
1
2
3
4
5
6
7
t, h
1
2

FIG. 5


T, °C
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36
t, min
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20
40
60
80
100
120
140
160
180
200
220
240
260

FIG. 6

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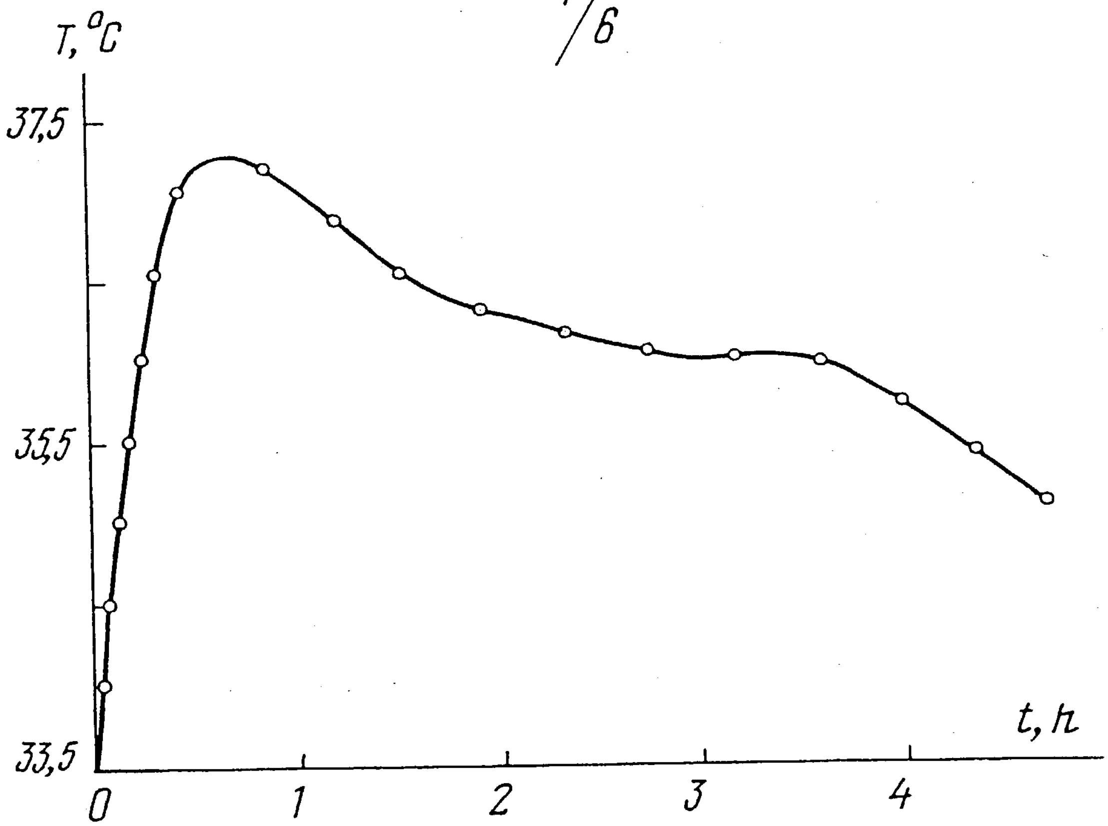

FIG. 7

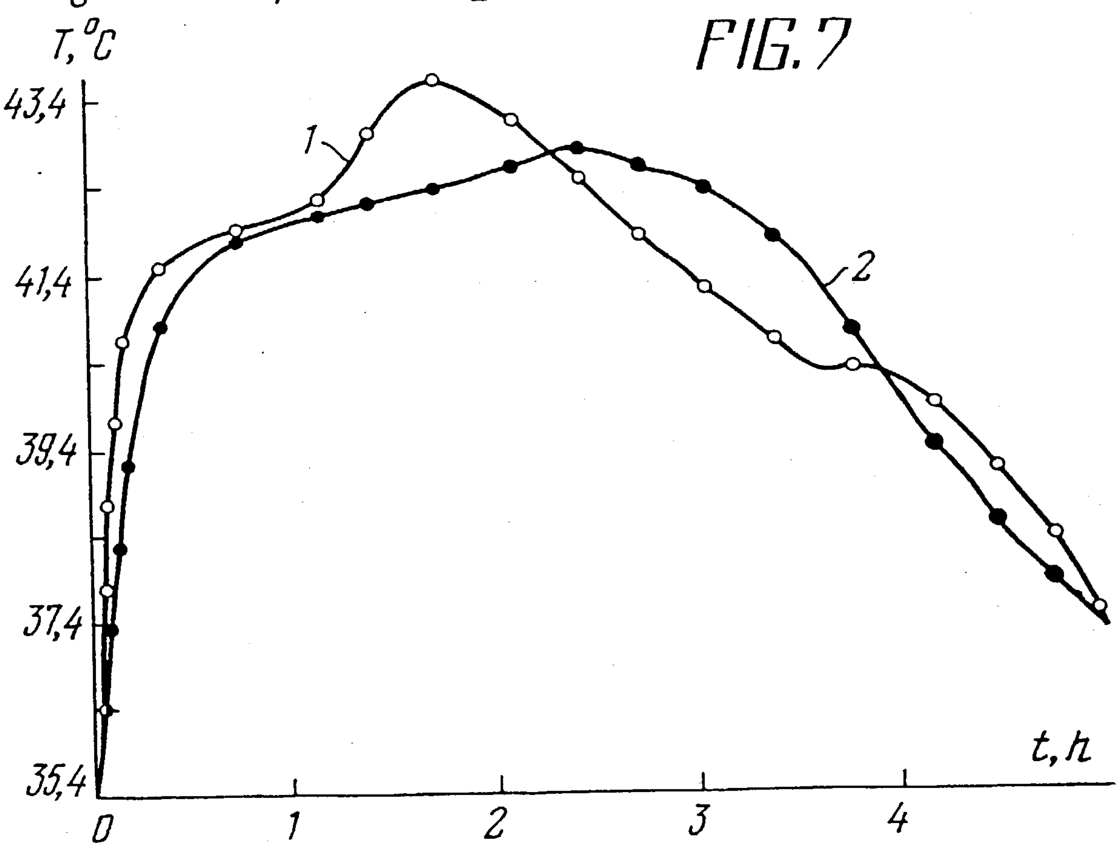

FIG. 8

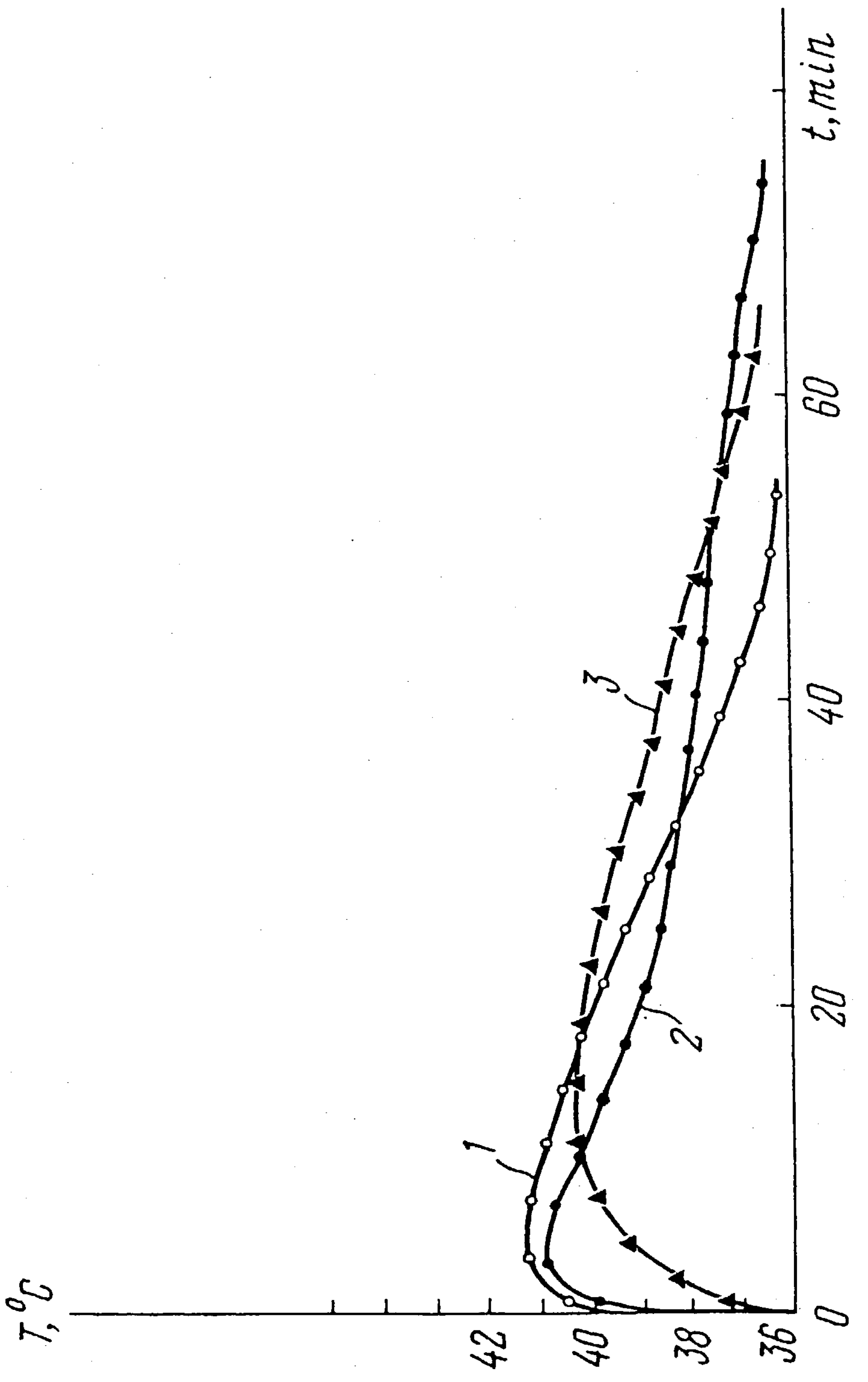

FIG.9

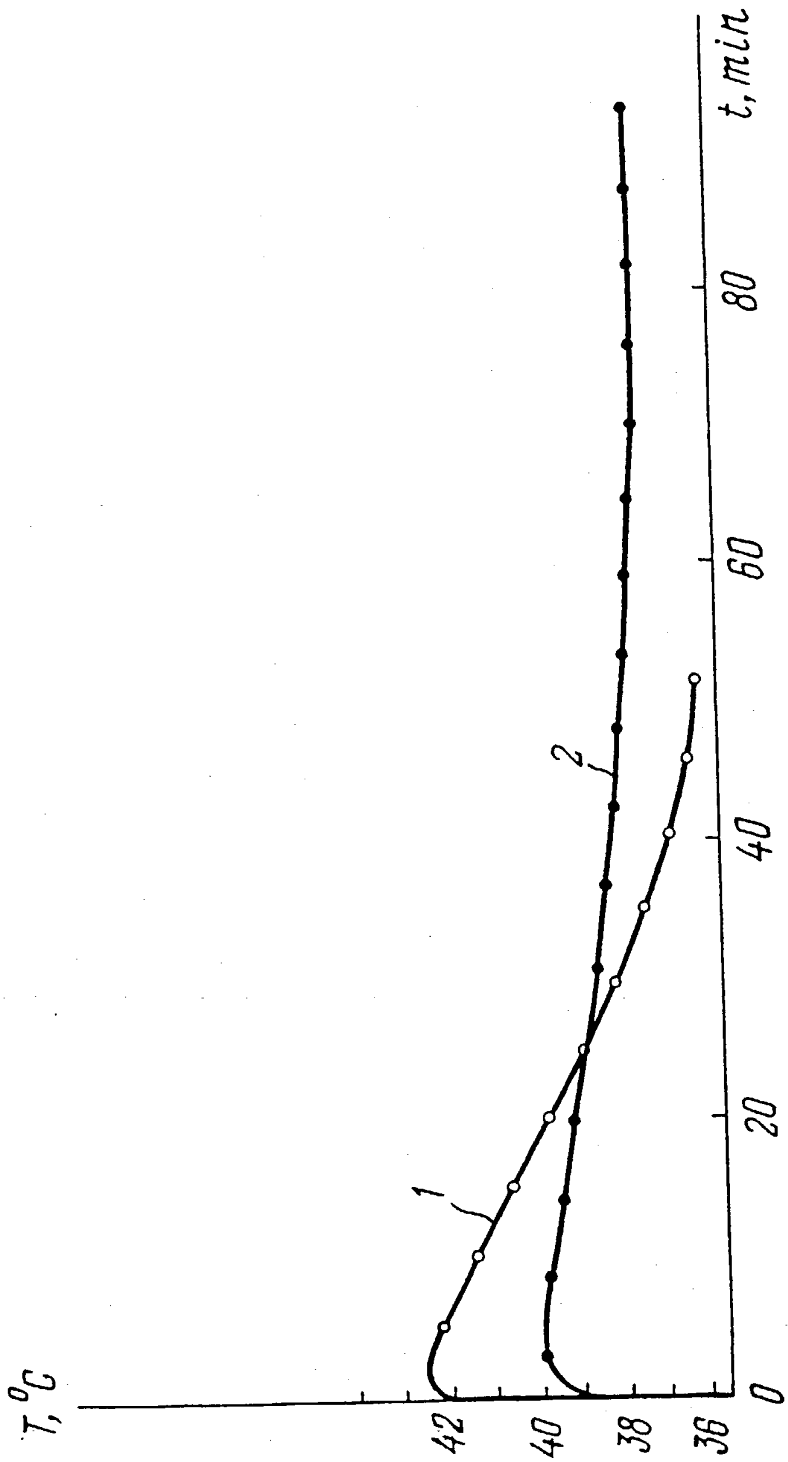

FIG.10

DECLARATION COMBINED WITH POWER OF ATTORNEY

Attorney Docket No. CM2215

As a below named inventor, I hereby declare that:

My residence, mailing address and citizenship are as stated below next to my name.

I believe I am the original and first inventor or inventors of the subject matter which is claimed and for which a patent is sought on the invention entitled Heat accumulating composition containing phase change material and crystallization modifier

the specification of which

(check	[]	is attached hereto.
one)	[x]	was filed on 13 August 1999 as United States Application No. or PCT International Application No. PCT/RU99/00294 and was amended on ______ (if applicable)

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. §1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s) — Priority Claimed

(Number)	(Country)	(Day/Month/Year Filed)	[] Yes	[] No

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

Application Serial No.	Filing Date	Application Serial No.	Filing Date

I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s), or §365(c) of any PCT International application designating the United States of America, listed below:

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (If applicable)

As named inventor, I hereby appoint the registered practitioners associated with customer number 27752 to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

SEND CORRESPONDENCE TO: Customer Number 27752

PCT/RU99/00294 10049200 .080702

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor Hartmut Hoehne
Inventor's signature
Date May 20, 2002
Residence Sulzbacher Str. 40-50, 65824 Schwalbach Am Taunus. Germany
Citizenship German
Mailing Address As Above

Full name of second inventor, if any Valentin Antonovich Vinogradov
Inventor's signature Valentin Antonovich Vinogradov
Date April 30, 2002
Residence Khoroshevskoe shosse. d.34,kv.38. 123007 Moscow. Russia
Citizenship Russian
Mailing Address As Above

Full name of third inventor, if any Valery Alexandrovich Dyatlov
Inventor's signature Valery Alexandrovich Dyatlov
Date April 30, 2002
Residence M. Levshinsky pereulok. d.12. kv.6, 119034 Moscow. Russia
Citizenship Russian
Mailing Address As Above

Full name of fourth inventor, if any Vladimir Alexandrovich Krenev
Inventor's signature Vladimir Alexandrovich Krenev
Date April 30, 2002
Residence Zelenodolskaya ulitsa. d.7. korpus 2, kv. 71.109377 Moscow, Russia
Citizenship Russian
Mailing Address As Above

Full name of fifth inventor Natalia Fedorovna Drobot
Inventor's signature Natalia Fedorovna Drobot
Date April 30, 2002
Residence Krasnoarmeiskaya ulitsa, d.25, kv.57, 125319 Moscow, Russia
Citizenship Russian
Mailing Address As Above

Full name of sixth inventor, if any Konstantin Sergeevich Gavrichev
Inventor's signature Konstantin Sergeevich Gavrichev
Date April 30, 2002
Residence Leninsky prospect, d.30. kv. 165. 117334 Moscow, Russia
Citizenship Russian
Mailing Address As Above

Full name of seventh inventor, if any Irina Zinovievna Babievskaya
Inventor's signature Irina Zinovievna Babievskaya
Date April 30, 2002
Residence prospect Vernadskogo, d.24a. kv.37. 117454 Moscow. Russia
Citizenship Russian
Mailing Address As Above

8 - 00

Full name of eighth inventor, if any Olga Anatolievna Noskova
Inventor's signature Olga Anatolievna Noskova.
Date April 30, 2002
Residence Elektrostal, ulitsa Mira, d.11a, kv.4 , 144007 Moskovskaya oblast, Russia
Citizenship Russian
Mailing Address As Above

9 - 00

Full name of ninth inventor, if any Elena Vladimirovna Bazhenova
Inventor's signature Elena Vladimirovna Bazhenova
Date April 30, 2002
Residence Dmitrovskoe shosse d.55, kv.33, 127238 Moscow, Russia
Citizenship Russian
Mailing Address As Above

10 - 00

Full name of tenth inventor, if any Viktor Sergeevich Vasiliev
Inventor's signature Viktor Sergeevich Vasiliev
Date April 30, 2002
Residence ulitsa Timiryazevskaya, d.7,kv 73, 125422 Moscow, Russia
Citizenship Russian
Mailing Address As Above

(DeclwithCustomerNumber.doc)
(Revised 11/12/01)

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CM2215F

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the U.S. National Phase Entry
Under 35 USC 371 from
International Application of
SULZBACHER, Hartmut Hoehne et al.
Int'l. Application No. PCT/RU99/00294
Filed in the RO/US on 13 August 1999
Entitled: *Heat Accumulating Composition*

ASSOCIATE POWER OF ATTORNEY

Assistant Commissioner for Patents
Box PCT
Washington, D.C. 20231

Dear Sir:

You are requested to recognize A. L. Winslow (Registration No. 48,586), K. McDow-Dunham (Registration No. 43,787), and J. B. Cunningham (Registration No. 43,962) of The Procter & Gamble Company, Cincinnati, Ohio, as Associate Attorneys to prosecute this application, to make alterations and amendments therein, and to transact all business in the Patent Office connected with the application or with the patent granted thereupon.

Please address all future communications to:

A. Winslow, Patent Attorney
Customer Number 27746

Respectfully submitted for Applicants,

By T. David Reed

T. David Reed
Agent for Applicant
Registration No. 32,931

Cincinnati, Ohio
29 January 2002
(513) 627-7025/FAX 627-6333